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CALCIA CLINKER AND ITS MANUFACTURING METHOD
[カルシア質クリカーその製造方法]
Fukuda et al.

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SPECIFICATION

1. Title of the Invention **CALCIA CLINKER AND ITS**

MANUFACTURING METHOD

2. Claims

(1)A calcia clinker which has much more the 1 wt. % of MgO with a principal component of CaO-MgO, with weight that contains using total weight of one kind or 2 or more kinds of Al₂O₃, B₂O₃, and TiO₂, and with weight containing 2 wt. % or less, with relative density 96% or more, and open porosity of 2% or less, and furthermore, with a thickness of the CaCO₃ layer by which the CaO was oxidized for the surface part, at 0.05-4.0μm.

(2) A calcia clinker according to Claim 1 wherein the thickness of the CaCO_3 layer which the CaO on the surface oxidized is $0.1-2\mu\text{m}$.

(3) A calcia clinker manufacturing method wherein with CaO-MgO as the principal component, there contains much more than 1 wt.% MgO , and using the total weight of one kind or 2 or more kinds of Al_2O_3 , B_2O_3 , and TiO_2 with relative density of 96% or more and open porosity of 2% or more, and heat within gas which contains a partial pressure of CO_2 15% or more, for 5 minutes or more at $380-830^\circ\text{C}$, making carbon dioxide of one part of CaO .

(4) A calcia clinker manufacturing method according to Claim 3 in gas which contains 15% or more partial pressure of CO_2 , heating for 5 minutes or more at $600-700^\circ\text{C}$.

(5) A calcia clinker manufacturing method according to Claim 3 or Claim 4 wherein the gas that contains CO_2 is at a partial pressure of 15% or less, and furthermore, the gas has 0.5-10% distilled water of 0.5-10%.

3. Detailed Explanation of the Invention

(Applied Field of the Invention)

This invention is related to calcia clinker which is superior for durability and manufacturing method.

/1

(Prior Art)

Recently, following the rationalization of industry, there has occurred continuous manufacturing and strengthening of degassing under conditions such as high temperatures. Consequently, there has been an increase in the use of fire resistant materials with materials that are chemically stable in great demand.

As material for flooring, conventionally there have been used salt-based fire retardants such as MgO and $\text{MgO-Cr}_2\text{O}_3$. In addition, there have been replacements from silicon based materials to those of salt-based retardants.

Principally, the salt based retardants used are from the MgO series. With respect to these, CaO is superior as a flame retardant and in slug immersion ability, and in addition, there is the point of being used to eliminate the Al_2O_3 within solutions, using MgO , and furthermore, they need no special handling so as to pose a reduced danger and can be used in the manufacture of bricks. Consequently, it is convenient to use the CaO series materials as fire

retardants, though the digestion and prevention issues present significant problems.

Methods for improving the digestion of high fire retardant materials which contain high amounts of CaO are principally known to be the following:

- a) Cover with the crystals of CaO according to various added materials
- b) Carbonize the CaO particle surfaces
- c) Coat with types of oil on the CaO particle surfaces

The method using a) among the 3 methods listed has seen various trials. For example, disclosed in Japanese Kokai S54-131612 is a method for improving the digestion proofing by including at total amounts of 10% or less one type or 2 or more types of Fe_2O_3 , CrO_3 , and TiO_2 with CaO or CaO-MgO, and especially the disclosure in S₅₉-³5060, as the principal material in CaO-MgO there has been used Fe_2O_3 , 0.4-1.2 wt. % or less, TiO_2 0.1-0.5 wt. % or less, and SiO_2 1.5wt. % or less.

There are known to be methods which use Al_2O_3 1.0 wt. % and 0.5-3.0 wt. % of Fe_2O_3 , TiO_2 , SiO_2 , and Al_2O_3 .

In addition with the method in (b), in the citation Amer. Ceramic Society Bulletin 49 (5), p. 531 (1970), there was heat treatment under CO_2 atmosphere of CaO sintered

materials, and when forming a CaCO_3 layer on the surface, there were reports that the digestability that resulted was good. Patent Kokai S56-88825 is known to have disclosed that there was improvement by heat treatment carbonization of CaO fire retardant particles with a fusion method.

(Problems that the Invention is to Solve)

However, in method (a) which added carbonization other than CaO and MgO, although the digestability proofing of the calcia clinker improved, there was formation of low fusion point compounds which damaged the fire retardability. For example, when adding Fe_2O_3 or Al_2O_3 (melting point 1447°C), $2\text{CaO}-\text{Al}_2\text{O}_3$ (melting point 1360°C) was formed.

In addition, with the method of (b), a carbonization processing occurred to give a high degree of purity for CaO. However, when using very pure CaO, certainly there was an improvement in digestability resistance from the carbonization, but mechanical failures occurred easy from friction, and from the separation of parts, there quickly results water saturation. Consequently, with this method, carbonization had to be significant to obtain a sufficient degree of digestability resistance, and the CaCO_3 layer became thick. Furthermore, when obtaining such a CaO, the

baked version had poor properties, and it was well known that the density did not improve, and in order to improve the digestability resistance a high proportion of carbonization was necessary, and with use, such as when using for fire-retardant bricks, the sintering ability became poor and there was a remarkable reduction in the strength for heat bending. Or, when the proportion of carbonization was high, the CaCO_3 decomposed, and there developed large spaces in the bricks. /2

(Means of Solving the Problems)

The goal of this invention is to provide calcia clinker which is superior for digestability resistance which is comprised of essentially CaO-MgO with no addition of other oxidized materials as a 3rd component.

The inventors researched the properties of calcia clinker (composition and properties) for conditions of carbonization with the result of discovering the appropriate properties of calcia clinker in order to solve the previously mentioned problems.

The calcia clinker which achieves the previously mentioned goal is a calcia clinker which has much more the 1 wt. % of MgO with a principal component of CaO-MgO , with weight that

contains using total weight of one kind or 2 or more kinds of Al_2O_3 , B_2O_3 , and TiO_2 , and with weight containing 2 wt. % or less, with relative density 96% or more, and open porosity of 2% or less, and furthermore, with a thickness of the CaCO_3 layer by which the CaO was oxidized for the surface part, at $0.05\text{-}4.0\mu\text{m}$.

and a calcia clinker wherein the thickness of the CaCO_3 layer which the CaO on the surface oxidized is $0.1\text{-}2\mu\text{m}$ and calcia clinker manufacturing method wherein with CaO-MgO as the principal component, there contains much more than 1 wt.% MgO , and using the total weight of one kind or 2 or more kinds of Al_2O_3 , B_2O_3 , and TiO_2 with relative density of 96% or more and open porosity of 2% or more, and heat within gas which contains a partial pressure of CO_2 15% or more, for 5 minutes or more at $380\text{-}830^\circ\text{C}$, making carbon dioxide of one part of and a calcia clinker manufacturing method in gas which contains 15% or more partial pressure of CO_2 , heating for 5 minutes or more at $600\text{-}700^\circ\text{C}$ and a calcia clinker manufacturing method wherein the gas that contains CO_2 is at a partial pressure of 15% or less, and furthermore, the gas has 0.5-10% distilled water of 0.5-10%. Assuming 3.65 (chemical ?), with a wt. % contents by weight of CaO , and b wt. % contents by weight of MgO , the following formula uses these values

$$\frac{\frac{BD}{3.37 \times a + \frac{3.65 \times b}{100}}}{100} \times 100 (\%)$$

In the formula BD is the specific gravity of calcia clinker with measurements based on the method which was determined by the Japan Chemical Technology Committee No. 124 Committee. In addition, the porosity is porosity measured by a method that was determined by the same committee. The properties of calcia clinker that are used in this invention are principally that the main components of the composition is CaO-MgO, and the composition contains much more than 1% OF MgO, and the contents is a combination of Fe₂O₃, Al₂O₃, B₂O₃, and TiO₂ of one kind or 2 or more kinds and that the amounts are 2 wt. % or less. Inn addition, for the physical properties, the relative density is 96% or less, and porosity is 2% or less. In this way, there can be countered the impurities which are generated with CaO and low fusion point compounds and according to the increase in relative density, it is possible to sufficiently demonstrate properties such as the strength of bending with heat for those compounds containing CaO. In addition, by making MgO be much more than 1 wt. % contents of the composition, and according to making the porosity 2% or less, it is possible to improve remarkably the resistance

to digestion compared with methods which carbonized conventionally by forming thin layers of CaCO_3 on the surface.

In order to form a CaCO_3 on the calcia clinker surface, it is necessary to heat treat under a CO_2 atmosphere. The necessary temperature range for carbonization is 380-830 °C, and especially desirable is the range 600-700 °C. With temperatures lower than 380 °C and higher than 830°C, the carbonization rate is slowed, and it is difficult to obtain a sufficiently thick CaCO_3 layer. For the processing temperature, according to the components of the calcia clinker, that is, the ratio of the MgO , there is an appropriate range, and it is desirable to select the conditions which obtain the desired digestion resistance within this range. For example, with calcia clinker which contains 90 wt. % of CaO , the temperature at which carbonization takes place has desirable processing at temperatures of 500 °C or above. It is possible for the CaCO_3 layer to form a desirable layer considering the processing time and temperature. For example, for calcia clinker with 97 wt.% CaO , if carbonizing at 500 °C for 10 minutes, 0.08 μm layer results, for 60 minutes, 0.2 μm , at 650 °C for 10 minutes, 0.2 μm results, and for 60 minutes, a layer thickness of 0.6 μm results.

/3

In addition, when carbonizing, there is an increase in the rate of carbonizing with the existence of water vapor in the gas which contains CO_2 , and the thickness of the CaCO_3 layer when doing the carbonized processing for the same time results becomes twice what it was before. Consequently, there is a reduction in the carbonization process according to contents of water vapor within the gas containing CO_2 , and it is convenient that it is possible to shrink the device for processing. The water vapor which is contained in the gas for carbonized processing can be a small amount, and with partial pressure, 0.5-10% is necessary. Less than 0.5% and an effect from the water vapor hardly occurs, and in addition, if more than 10%, there is no effect.

The digestion resistance for the carbonized calcia is different depending on the thickness of the formed CaCO_3 layer, and a thickness of 0.05-4 μm is necessary. Especially desirable is a thickness of 0.1-2 μm . When the thickness of the CaCO_3 layer is thinner than 0.05 μm ,

①It is difficult to obtain a sufficient resistance to digestion.

②the strength of the CaCO_3 layer is low, and breakage is easy from friction among calcia particles

③ The rate of carbonization slows as the CaCO_3 layer becomes thick, and at a thickness of 4 μm , it is necessary

to process for several hours. In addition, even with the thickness at $4\mu\text{m}$ or above, the water salvation property tops out, and consequently making the CaCO_3 layer thicker is useless, and is not economic.

④ The proportion of impurities in the CaCO_3 layer becomes greater with thicknesses above $4\mu\text{m}$ or more, and the sintering capability when manufacturing fire retardant bricks is reduced.

⑤ Using calcia clinker, when the non-sintered fire retardant bricks are manufactured, when using at high temperature, the CaCO_3 of the clinker surface decomposes and CO_2 is generated. At this time, if the CaCO_3 is thicker than $4\mu\text{m}$,

the spaces between the clinker and the carbon from the decomposition of the CaCO_3 become larger, and the brick strength becomes weaker from clinker separation.

The thickness of the CaCO_3 layer is determined using a Hitachi standard MSM-4. Figure 1 shows the CaO before carbonization, and Figure 2 shows after carbonization with CaO at 97 wt.% and MgO , both photographs taken with an electron microscope of the clinker. The carbonized clinker has a uniform multicrystalline surface of CaCO_3 , with no peaks, and it is understood that the generated CaCO_3 layer is dense. That this layer is CaCO_3 is confirmed according to

X-ray diffraction. In addition, Figure 3 shows a clinker after carbonization, containing CaO 69.3 wt. % and MgO 30.1 wt. %. The arrow ① is the part of CaO which carbonized, and the arrow ② is the part of MgO. The thickness of the CaCO₃ layer is obtained according to the quantity of CO₂ from vapor decomposition or chemical decomposition. Figure 4 shows the relationship between the carbonization rate and the particle diameter (radius) when carbonizing a clinker containing 97 wt. % CaO. The particle diameter shows an average diameter of the 3 axes of the clinker (short axis diameter, long axis diameter, and height [thickness] as an average value), and in addition, the carbonization rate, it is shown, changes as the proportion of CaCO₃ in CaO. Actually, the manufacture of the carbonized calcia clinker yields in a tank the clinker after sintering using ? and after cooling and supplying gas containing CO₂ to the clinker and with cooling it is thought to perform the carbonization of the clinker's surface.

[Embodiment]

Next, there is shown embodiments and comparative examples of this invention. Moreover, digestion resistance experiments using the embodiments and the comparative

examples are performed with that method that uses clinkers whose particle diameters are 2.00-4.76mm at 25 °C in 70% air and leaves it standing for 2 weeks, and by determining the increase rate in weight during this time, the digestion resistance is evaluated.

/4

Embodiment 1 and Comparative Example 1

With the raw materials of $\text{Ca}(\text{OH})_2$ and $\text{MG}(\text{OH})_2$ obtain a calcia clinker. Using one part, in gas which is CO_2 partial pressure, carbonize for 60 minutes at 700 °C. Perform an evaluation of this carbonized processed experimental material and non-carbonized experimental material and evaluate the digestion resistance. Table 1 shows the chemical composition, relative density, porosity rate, and digestion resistance evaluation results. In addition, the thickness of the CaCO_3 layer for the experimental material that was carbonized was, from electron microscopic observations was No. 6 0.6 μm , and experimental material No. 7 0.2 μm .

From Table 1 it is understood that this invention's calcia clinker has superior digestion resistance.

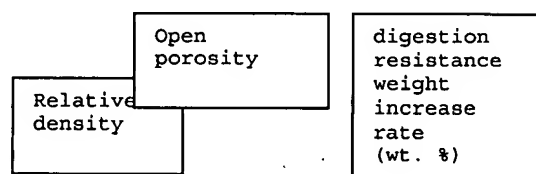


Table 1

Chemical
composition
(wt. %)Experimental
material No.

Comparative experiment	試料No.	化学組成 (重量%)						Other		密度 (%)	透氣孔率 (%)	耐消化性重 量增加率 (重量%)
		Ca O	Mg O	Fe ₂ O ₃	Al ₂ O ₃	B ₂ O ₃	Ti O ₂					
Embodiment	1	88.70	0.50	0.05	0.10	0.10	> 0.01	—	0.9	96.3	3.6	1.32
	2	99.20	0.20	0.03	0.10	0.10	> 0.01	—	0.5	96.5	1.2	0.88
	3	97.30	1.75	0.05	0.09	0.01	> 0.01	—	0.8	96.2	1.0	0.53
	4	69.32	30.06	0.04	0.08	0.12	0.01	—	0.4	97.1	1.7	0.09
	5	99.20	0.20	0.03	0.10	0.01	> 0.01	0.08	0.5	96.3	1.1	0.03
	6	97.20	1.75	0.05	0.09	0.01	> 0.01	0.10	0.6	96.5	1.1	0.005
	7	69.60	30.06	0.04	0.08	0.12	0.01	0.03	0.4	97.0	1.5	0.001

particle size: 2.00-

4.76mm

/5

Embodiment 2

Carbonize the clinker of 2.00-4.76mm particle size using experimental materials No. 3 and No. 4 shown in Table 1 at 95% CO₂ partial pressure with at 700 °C. The values of the relative density of the processed clinker and the open porosity changed compared to the unprocessed experimental materials when processed for 3 hours. Table 5 shows the relationship between the processing time and the thickness of the formed CaCO₃ layer. From the results in Table 5 the CaCO₃ layer became thicker during the processing period and with this increase the rate of carbonization became slower, and it is understood that the rate of carbonization was different according to the MgO content.

Next, perform a low digestion experiment for No. 3 and No. 4 clinker which were processed in the same way. Figures 6 and 7 show the relationship between the thickness of the processed CaCO₃ layer and the weight increase rate. Moreover, there is shown the experimental materials No. 3 and 4 values for no carbonization of Comparative Example 1 for values of weight increase rate with CaCO₃ layer thickness at 0. From these results, with this invention, according to the formation of the CaCO₃ layer of 0.05μm thickness, the weight increase rate for non-processed material in 10

minutes was 1, with $0.4\mu\text{m}$ for 100 minutes it was 1, so it is understood that there was a significant improvement in digestion resistance for the calcia clinker.

The particle diameter of experimental material No. 3 which is shown in Table 1 was $2.00\text{--}4.76\mu$ for CO_2 partial pressure at 95% and for every temperature at 380, 200, 350, and 870 °C, and processed for 60 minutes and a digestion resistance experiment was performed for all experimental material. Table 8 shows the results for Embodiment 3 and Comparative Example 2. The temperature range from these experiments which is effective for carbonization is understood to be 380-830 °C.

Embodiment 4

The particle diameters for experimental material No. 3 which were shown in Table 1 was $2.00\text{--}4.76\mu\text{m}$ for a partial pressure of CO_2 with a clinker was 95% with carbonization for 60 minutes at all the temperatures of 400, 500, 600, 700, and 800, and a resulting digestion resistance experiment performed, however, the materials were left standing for 4 weeks. The results are shown in Table 2. From these results, the processed temperature was effective at 600-700 °C.

Table 2

Processing temp (°C)	Weight increase rate (wt. %)
400	0.49
500	0.26
600	0.13
700	0.08
800	0.18

Embodiment 5 and Comparative Example 3

The particle diameters for experimental material No. 3 which were shown in Table 1 was 2.00- 4.76 μ m for partial pressures of CO₂ with a clinker of 2, 15, 50, and 95% with carbonization for 60 minutes at all the temperature of 600 °C and the digestion resistance was evaluated. There

was analysis using a gas analyzer with carbon dioxide CO₂ partial pressure 99.95%. The results are shown in Table 3. With the CO₂ partial pressure 15% and above, there was effective carbonization and an improvement in digestion resistance was seen.

Table 3

	CO ₂ (%)	Weight increase rate (wt.%)
Comparative	Not processed	0.53
Example 3	2	0.55
Embodiment 5	15	0.01
	50	0.008
	95	0.003

Embodiment 6 and Comparative Example 4

The particle diameters for experimental material No. 3 and No. 4 which were shown in Table 1 was 2.00- 4.76 μ m for a partial pressure of CO₂ with a clinker was 95% with carbonization for 60 minutes at all the temperatures of 700 °C. The results of the effect on thickness of the CaCO₃ layer with water vapor and processing are shown in

Table 4. From the table, according to the existence of water vapor in the gas containing CO₂ the CaCO₃ layer became thicker and there was obtained a CaCO₃ layer of sufficient thickness with a short processing time. However, there was no effect when the amount of water vapor increased.

/6

Table 4

	CO2 partial pressure (%)	Water vapor partial pressure (%)	CaCO3 layer thickness	
			No. 3	No. 4
Comparative	97	0.0	0.58	0.22
Example 4	96	0.1	0.55	0.23
Embodiment	93	0.9	1.10	0.44
6	96	1.8	.94	0.41
	85	10.0	0.88	0.50
Comparative	78	14.8	1.00	0.56
Example 4				

Embodiment 7 and Comparative Example 5

Table 5 shows the processing results for materials No. 2, No. 3, and No. 4 shown in Table 1 with particle diameters 2.00-4.76mm. Table 5 also shows the thickness of the CaCO_3 layer at this time. Using a shaker of diameter 9cm and height 13cm with the No. 8-11 experimental materials there was carbonization using 200g for 30 minutes. The amplitude was 5cm, and movements done at 240 times/minute. Digestion resistance was evaluated after shaking for the experimental materials. The results are shown in Table 6. The mechanical impact with a thin CaCO_3 layer was weak. However, with a thickness of around $0.1\mu\text{m}$, the weight increase rate compared to the materials that were not carbonized was reduced to 1 part in 10. In addition, even with separation of the CaCO_3 layer, the clinker with high MgO content was superior in digestion resistance.

Table 5

After carbonized processing experimental materials	Before carbonized processing No.	CO_2 partial pressure (%)	Processing time (minutes)	CaCO_3 layer thickness (μm)
--	---	---	---------------------------------	--

No.				
8	3	95	3	0.03
9	2	96	10	0.09
10	3	96	10	0.09
11	4	94	30	0.11

Table 6

	Experimental Materials No.	Weight increase rate (wt. %)
Comparative Example 5	2	0.88
	3	0.53
	4	0.09
	8	0.22
	9	0.09
Embodiment 7	10	0.05
	11	0.001

Embodiment 8 and Comparative Example 6

Composition using the following particles for clinker of the same chemical composition as material No. 3 shown in Table 1.

3.36-2.00mm	50g
2.00-1.00mm	50g
1.00-0.25mm	50g

With a CO₂ partial pressure of 97% carbonized at 700 °C. By changing the processing time, there was obtained the particle distribution. Using an electron microscope, the results in Table 7 were obtained for the thickness of the CaCO₃ layer. With respect to these materials No. 12-16, add 100g of MgO powder whose particle diameters were less than 0.25mm as a binder for ethyl silicate, and insert metal material that was rectangular at 25 x 125mm and apply pressure of 1 ton/cm². Bake for 2 hours at 1700 °C. Measurements were taken as shown in Figure 9 of the bending strength while heated at 1200 °C for bricks. Figure 10 shows the relationship of the bending strength of the bricks with heat and the thickness of the CaCO₃ layer. The vertical axis of the figure shows the relative values with values of 1.0 for the bending strength under heat for bricks that were formed using CaO with no processing using material NO. 12. From the table, if the thickness of the CaCO₃ layer exceeds 4μm, the strength of the bricks is rapidly reduced. /7

Table 7

	Experimental material No.	Thickness of CaCO_3 layer (μm)
Comparative Example 6	12	0 (not processed)
Embodiment 8	13	0.5
	14	1.7
	15	3.3
Comparative Example 6	16	4.5

[Effect of the Invention]

According to this invention, there is obtained calcia clinker which is superior in digestion resistance. In addition, there is superior bending strength under heat for fire retardant bricks which use this clinker.

4. Brief Explanation of the Drawings

Figure 1 and Figure 2 are electron microscope photos which show the crystal manufacture of clinker before processing

and after processing, Figure 3 is an electron microscope photo which shows the crystalline structure of the surface of the clinker after carbonization, Figure 4 is a graph which shows the relationship of the particle diameter of the clinker and the carbonization rate, Figure 5 is a graph which shows the relationship of the thickness of the CaCO_3 layer and the processing time, Figures 6 and 7 are graphs which show the relationship of the thickness of the CaCO_3 layer and the weight increase rate, Figure 8 is a graph which shows the relationship of the carbonization processing temperature and the weight increase rate, Figure 9 is an explanatory diagram of the bending strength under heat measurement device, and Figure 10 is a graph which shows the relationship of the thickness of the CaCO_3 layer and the bending strength under heat.

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Agent Patent Attorney Komatsu Hideoka

图 1



图 2



图 3

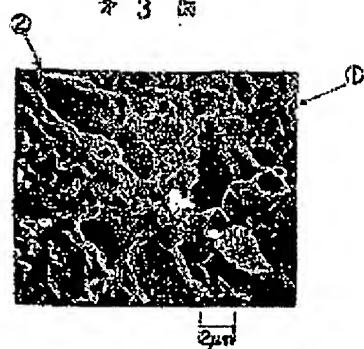


図 4

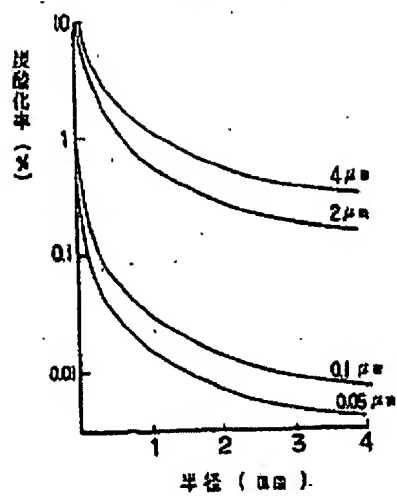


図 5

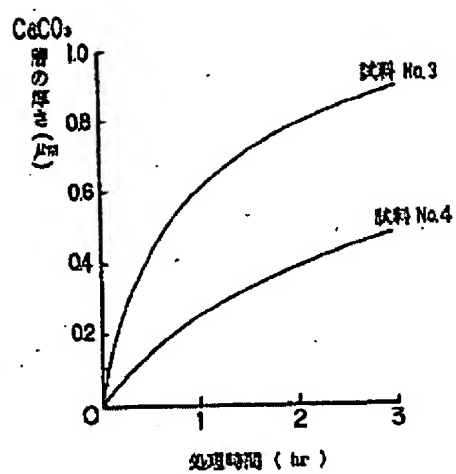


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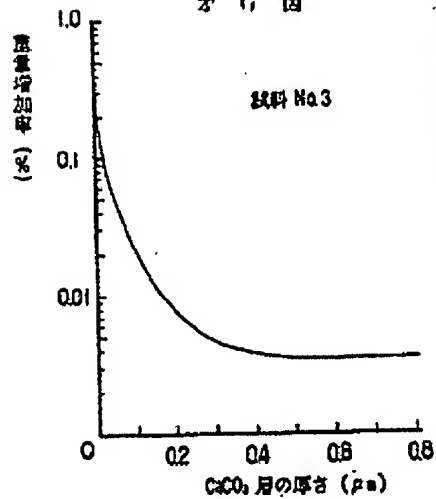
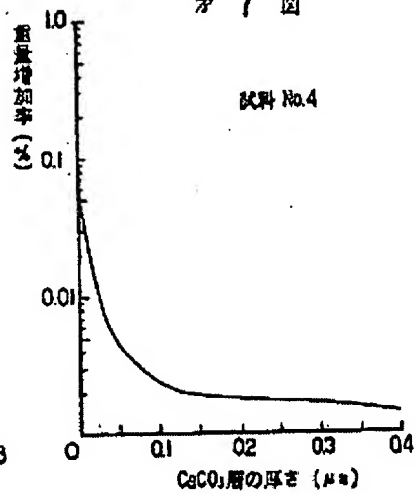
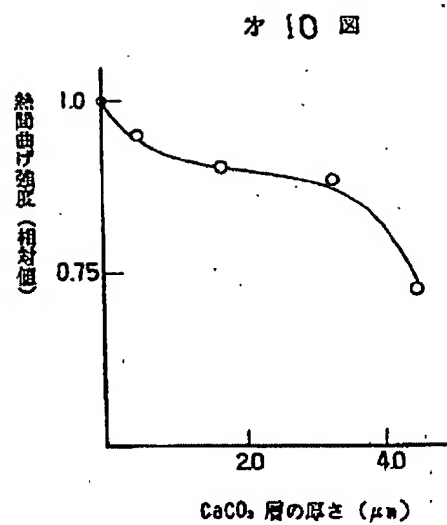
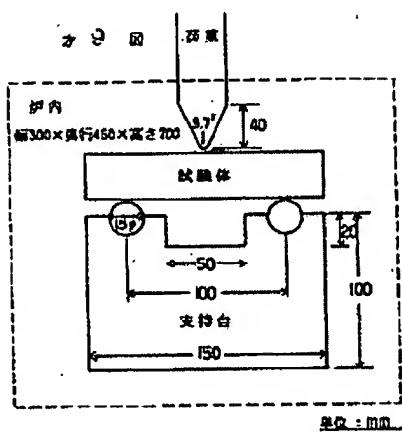
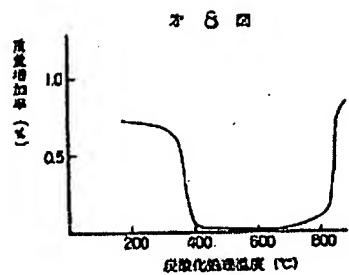


図 7





Written Amendment (Voluntary)

June 12, 1985

To: Japan Patent Office

1. Disclosure Matter

S60-95226

2. Title of the Invention

Calcia clinker and its manufacturing method

3. Person making amendment

Relationship to matter Applicant

Name or title Shin Nihon Chemical

4. Agent

Komatsu Hideoka

5. Amendment directive date (voluntary)

6. Amendment Subject

Detailed explanation within specification

7. Amendment Contents

(1) Amend "impact easy" of p.6 line 7 in specification to "when receiving impact, separation easy for parts which were carbonized"

(2) Amend "carbonization (missed spelled)" of specification p.17 lines 4-5 to "carbonization"

(3) Amend "... 380 °C (more than Embodiment 3)" in Specification p.18 line 9 to "380, 500, 600, 700, and 830 °C (more than Embodiment 3)"

/10